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Development of "DUCRETE"

Paul A. Lessing

Lockheed Idaho Technologies Company

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Development of "DUCRETE"

INEL-94/0029

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Depleted Uranium Recycle Project

ABSTRACT

This interim report covers theoretical and experimental aspects of a series of scoping tests using depleted uranium oxide pieces as aggregate in portland cement to form concrete (DUCRETE). DUCRETE is expected to provide a high integrity material suitable for shielding in spent nuclear fuel containers or for direct disposal in a low-level waste repository. The uranium oxide would be produced by conversion of depleted UF_6 stored by the Department of Energy.

Depleted UO_2, U_3O_8, iron-enriched basalt (IEB), and quartz-type gravel (reference) were used as large aggregate to fabricate concrete. Concrete with UO_2 aggregate had densities up to 6.33 g/cm^3; theoretical calculations show that at this density spent nuclear fuel shielding walls can be less than 10 in. thick (at a 200 mrem/hr limit). The compressive strengths of DUCRETE mixtures were in the range typical of construction grade concretes (3,000 to 6,000 psi) for a curing time of 7 days. Compressive strength values were somewhat dependent upon the shape and roughness of the aggregate. DUCRETE has compressive strengths slightly lower (20.6% average) than the equivalent gravel-aggregate concrete, while the flake-like morphology of the IEB aggregate led to strengths lower (33.7% average) than those of the gravel-aggregate concrete.

No deleterious interactions between the $U0_2$ aggregate and the portland cement were visible after 7 days at room temperature. Exposures to elevated temperatures (90 to 150°C) did not cause a significant decrease in mean compressive strengths, while mean tensile strengths increased over a 28 day cure. Due to limited available aggregate, only two samples per data point were tested. Thus, the statistical confidence in the data is poor.

Exposure to 250°C for 14 days weakened (gravel aggregate), cracked (U_3O_8 aggregate), or disintegrated (UO_2 aggregate) the concrete. Experiments are underway to determine the mechanism of this degradation. Additional experiments are being conducted to incorporate urania powders directly into IEB melts to inexpensively form a hard, dense aggregate with urania loadings up to 97 wt%.

ACKNOWLEDGMENTS

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Development of "DUCRETE"

1.0 INTRODUCTION

The Department of Energy (DOE), Office of Environmental Restoration and Waste Management, has chartered a study of alternative management strategies for the depleted uranium (DU) stored throughout the DOE complex. The DOE currently has a DU inventory of about 555,000 metric tons of uranium hexafluoride, mostly stored in 10 and 14 ton cylinders at the DOE gaseous diffusion plants. Since UF_6 is a relatively unstable compound, and the steel containers will eventually corrode, indefinite storage of the material is not a long-term option. Consequently, DOE is sponsoring work to evaluate disposal options and possible beneficial uses of the depleted uranium.

One approach is to use depleted uranium oxide as a heavy aggregate in portland cement based concrete. This concrete, named "DUCRETE," can be a stable, final waste form or be used as a structural material in spent fuel storage containers. The concept behind DUCRETE is to synthesize an aggregate from uranium oxide that will replace the conventional aggregate in the concrete. Uranium oxides are inherently stable and, when combined in a cement matrix, are expected to provide a high integrity material suitable for shielding purposes in spent nuclear fuel containers or for direct disposal in a low-level waste disposal site.

Heavy aggregate concretes have been used as structural shielding against ionizing radiation. Traditional heavy aggregate concretes use compounds like barite ($BaSO_4$, density = 4.5 g/cm^3) or magnetite (Fe_3O_4, density = 5.2 g/cm^3) as replacements for the coarse aggregate and sand in concrete. The resulting concretes have densities of about 3.4 to 4.8 g/cm^3 (210 to 300 lb/ft^3); construction grade concrete has a typical density of 2.2 to 2.4 g/cm^3 (140 to 150 lb/ft^3) and a compressive strength of 24 to 41 MPa (3,500 to 6,000 psi).

Since the theoretical density of UO_2 is nearly 11 g/cm^3, it was estimated that a concrete density of about 6.5 to 7.0 g/cm^3 would be possible. If U_3O_8 or UO_3 were used, the resulting concrete densities would be lower. If a density of 6.0 to 7.0 g/cm^3 was realized, the material would have unique shielding advantages for spent nuclear fuel storage containers. Even if not used for spent fuel storage, the high uranium oxide loadings would lower the cost of disposal because of the high volumetric waste loading.

To test these theoretical predictions, a series of scoping tests were undertaken to determine the behavior of various types of uranium oxide in a cement matrix. Additional tests were conducted to determine if uranium oxide powder could be mixed with basalt and sintered to produce an aggregate with high concentrations of uranium.

This interim report provides data on the compressive strength and tensile strength of depleted uranium concrete fabricated from UO_2 and U_3O_8. Data on chemical stability at high temperatures in the presence of moisture are also presented. Lastly, preliminary data on the properties of the concrete fabricated with basalt aggregates are presented.

2.0. THE ART OF CONCRETE MIXTURES

Evaluation of concrete literature[1] showed that ordinary concrete mixes aged between 3 and 7 days generally have strengths between 3,000 and 5,000 psi when using cement:aggregate values between 1:3 and 1:7 (with the water/cement ratio, by weight, about 0.4). Aging for a year under favorable conditions may result in strength values as high as 10,000 psi. High-strength concretes (up to 12,000 psi) generally are made with special compositions [high alumina cement, finely ground cement, pozzolanic (e.g., fly ash, fumed silica) additives, etc.].

Based upon Figures 1 and 2 (taken from Orchard[1]), we proposed to begin with a water/cement ratio of 0.4 and, if the mixture was dry, increase it to a ratio of 0.45. If workability was still a problem, for a given cement/aggregate mixture, then the water/cement ratio could be increased to approximately 0.6.

Various degrees of workability are described in Table 1. Since there was a concern that the highly dense UO_2 aggregate would settle to the bottom of cast structures, it seemed undesirable to have a high degree of workability. From Table 1, workability varying from very low (0-1 in. slump) to medium (1-4 in. slump) is appropriate. Since we selected a preferred water/cement ratio of about 0.4, the aggregate/cement ratio can be adjusted to achieve the needed workability. This is shown in Figure 3.

The aggregate/cement ratio will vary for a given screen analysis. The numbers 1,2,3,4, on the curves in Figure 3 are for a screen analysis as shown in Figure 4 and its associated table. The higher the curve's number is, the higher the weight of its fine fractions. In these curves and table, the aggregate includes both the sand and the gravel.

For a maximum aggregate size of 3/8 in., the aggregate/cement ratio varies between approximately 2.5 and 4.0 for a water/cement ratio of 0.4, and between 3.5 and 5.0 for a water/cement ratio of 0.6. For a given screen fraction of aggregate, better workability is achieved by decreasing the aggregate content or increasing the water/cement ratio. For DUCRETE, there is a choice between increasing the water content (slightly decreasing strength) or reducing the UO_2 content (decreasing the shielding capability).

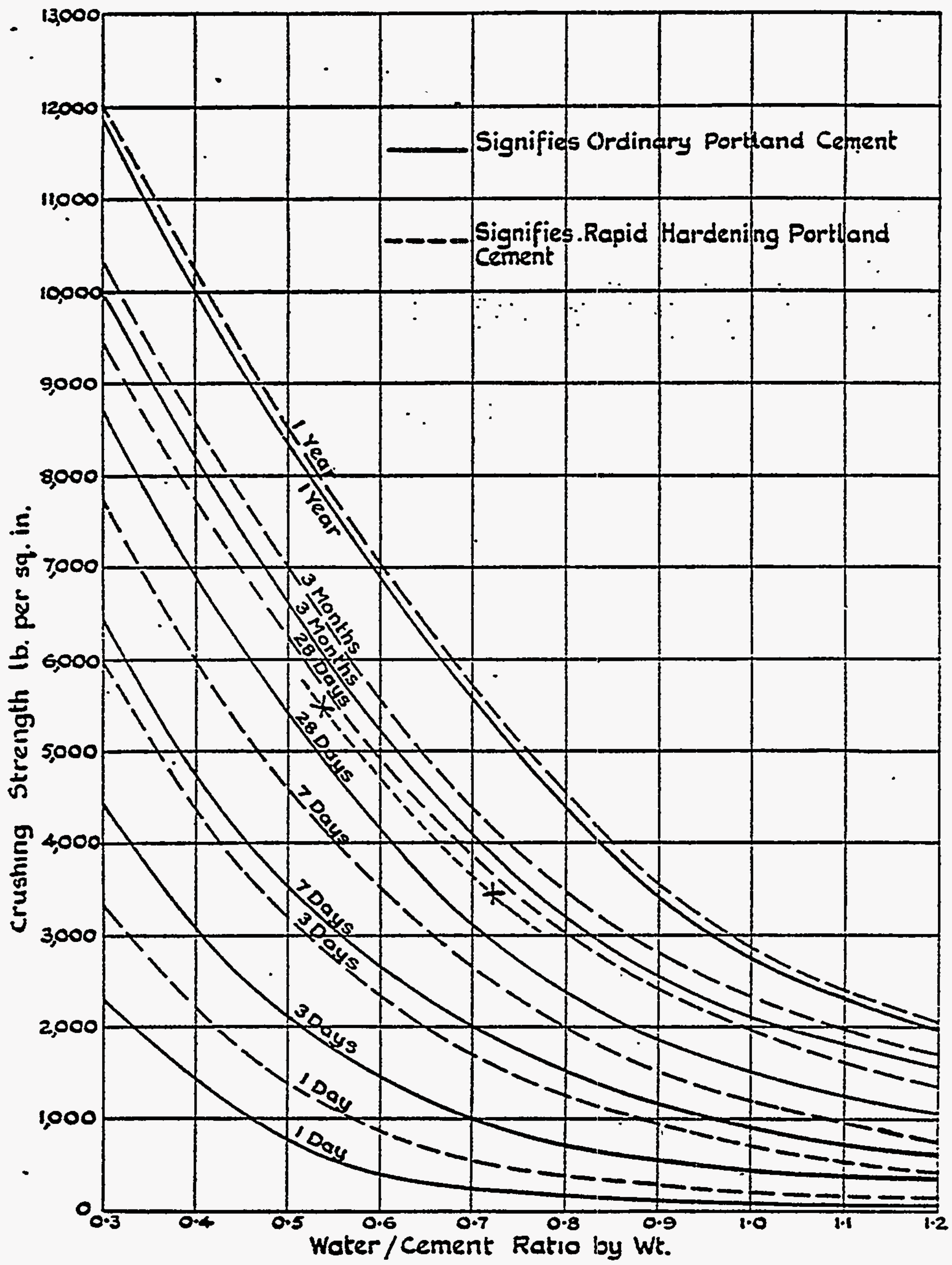


Figure 1. Relation between crushing strength and water/cement ratio for fully compacted concrete. (Orchard,[1] Figure 5.11)

For a water/cement ratio of 0.4 and a Type 4 screen analysis, the workability is "very low" for an irregular gravel aggregate/cement ratio of 2.8. For workability to improve to "medium", the aggregate/cement ratio has to decrease to about 2.2 (more cement would be needed). Alternately, if we want to maintain "low" workability, the water/cement ratio must rise to about 0.7-0.8 so as to have an aggregate/cement ratio of 6.5.

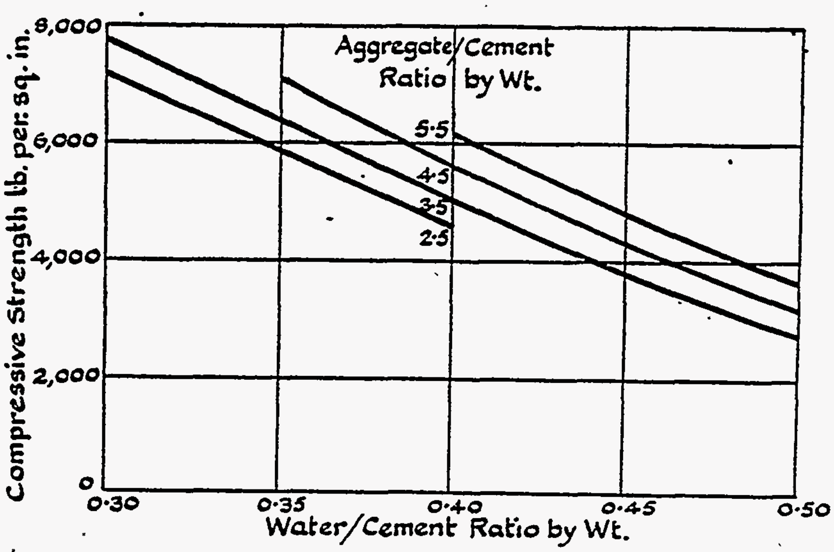


Figure 2. Typical relationship between compressive strength and water/cement ratio for various aggregate/cement ratios. (Orchard,[1] Figure 5.2)

Table 1. Suggested degrees of workability for different placing conditions. (Orchard,[1] Table 5.XIX)

Proposed use and placing conditions	Degree of Workability	Compacting factor: Small apparatus, ⅜ in aggregate	Compacting factor: Small apparatus, ¾ in aggregate	Compacting factor: Large* apparatus 1½ in aggregate	Very approx. slump (in)
Extremely intensive vibration on vibrating table possibly with top pressure	Extremely low	0·65	0·68	—	Nil
Intensive vibration of simple sections. Mechanical compaction of roads	Very low	0·75	0·78	0·80	0–1
Vibration of simply reinforced sections. Roads and slabs compacted by hand operated vibrating machines, mass concrete compacted with vibration	low	0·83	0·85	0·87	¼–2
Hand compaction of simply reinforced sections. Vibration of heavily reinforced sections. Hand compaction of roads and slabs	Medium	0·90	0·92	0·935	1–4
Hand compaction of heavily reinforced or complicated sections	High	0·95	0·95	0·96	2–7

* Omitted from British Standard. *see* Vol. 2.

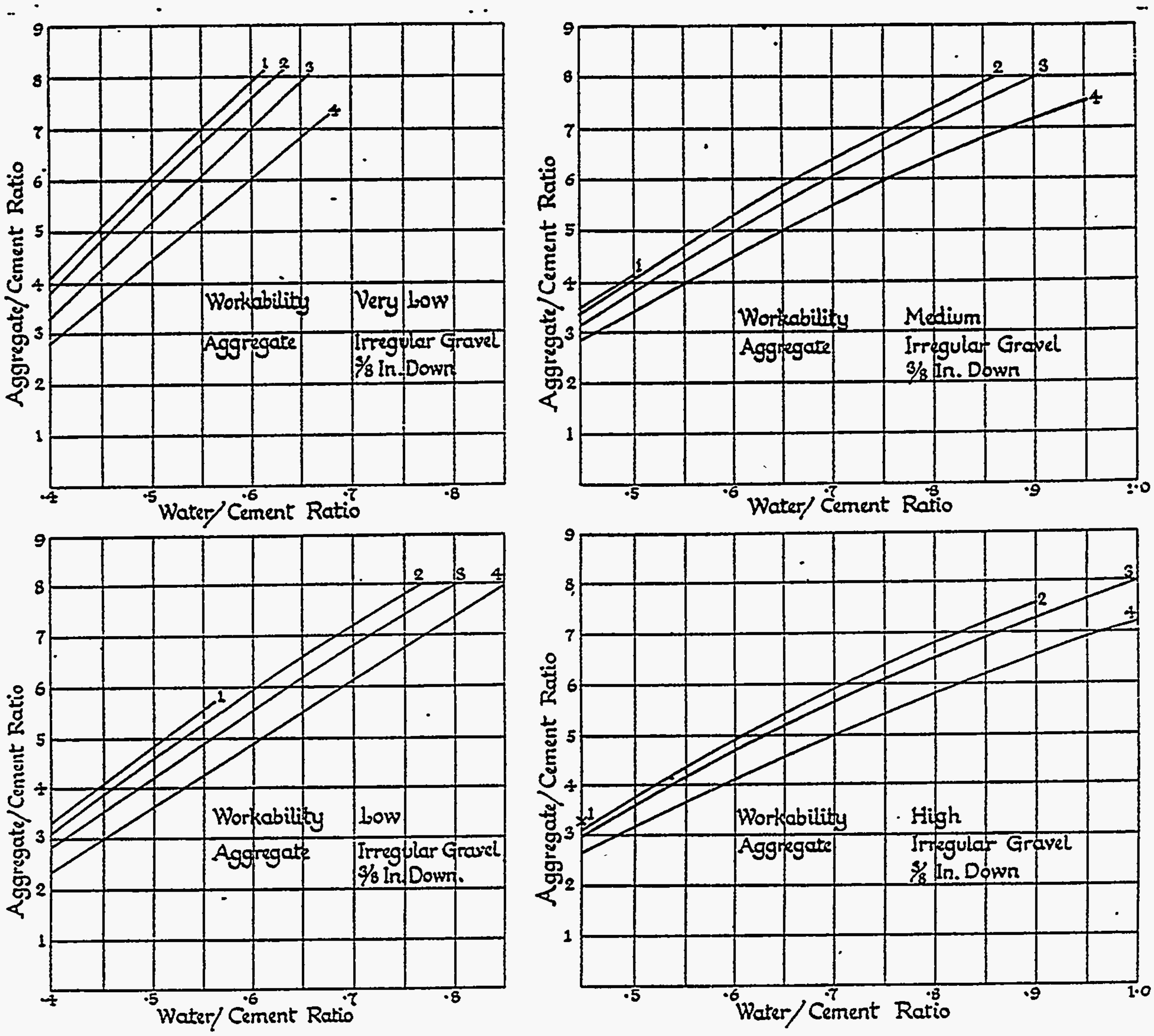
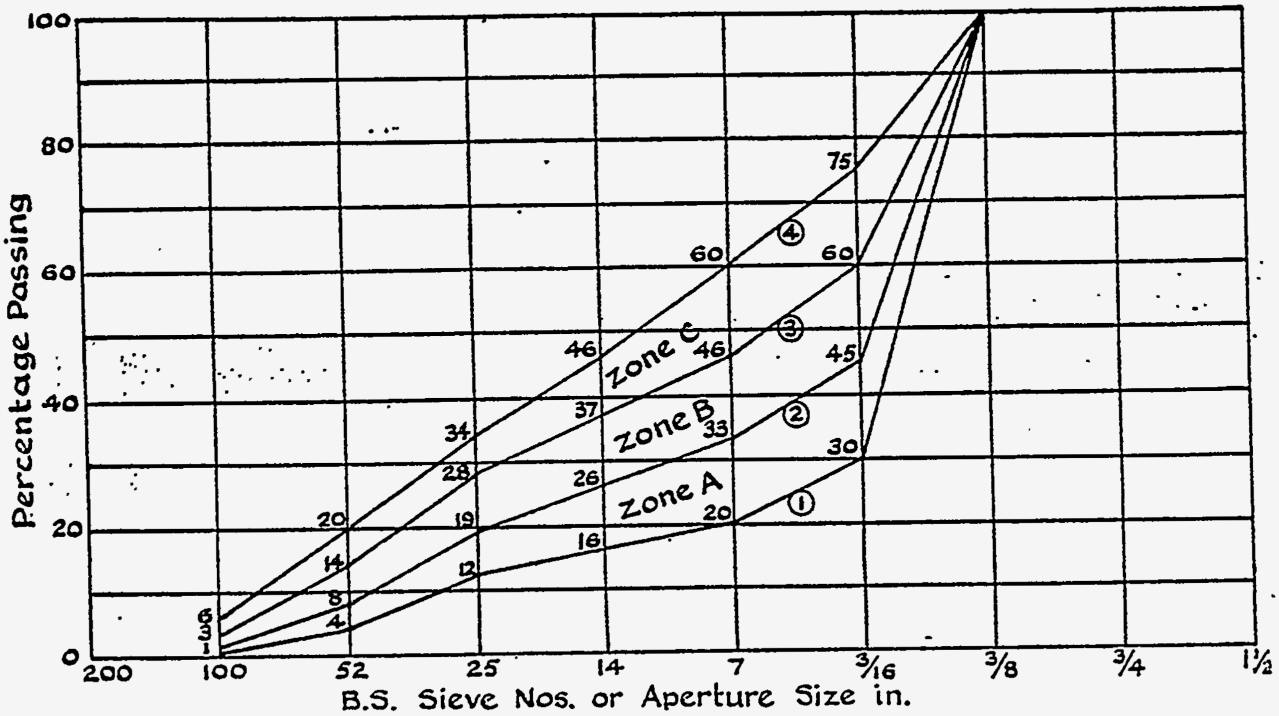


Figure 3. Workability as a function of water/cement and aggregate/cement ratios. (Orchard,[1] Figure 5.12)

Radiation shielding calculations were performed at the Idaho National Engineering Laboratory[2] for cement:sand:UO_2 aggregate mass ratios between 1:2:3.5 and 1:2:24. Based upon a UO_2 density of 10.96 g/cm^3, compared to a calcite aggregate density of 2.7 g/cm^3, an equivalence can be established as shown in Table 2. Approximate theoretical concrete densities were calculated for the various batch formulas used in the shielding calculations (using the heavy urania aggregate) as shown in Table 3. The cement density was assumed to be 3.1 g/cm^3 and the sand density to be 2.645 g/cm^3; the uranium oxide was assumed to have a sintered density of 95% of theoretical (10.41 g/cm^3). The molar ratio of bound water to silica in the cement was assumed to be 2.25, and all the water was assumed to be



Sieve Size	⅜ in							
	Percentage passing for curve no.				Percentage retained on for curve no.			
	1	2	3	4	1	2	3	4
6								
3								
1½								
¾								
⅜	100	100	100	100				
3/16	30	45	60	75	70	55	40	25
7	20	33	46	60	10	12	14	15
14	16	26	37	46	4	7	9	14
25	12	19	28	34	4	7	9	12
52	4	8	14	20	8	11	14	14
100	0	1	3	6	4	7	11	14
						1	3	6

Figure 4. Grading curves for 3/8 in. maximum size aggregate. Associated table gives sieve analysis for the various aggregates in the figure. (Orchard,[1] Figure 5.6)

Table 2. Equivalence ratios for batch formulas.

cement:aggregate --->	cement:sand:gravel --->	cement:sand:UO_2 chunks
1 : 3.5	1 : 2 : 1.5	1 : 2 : 6
1 : 5	1 : 2 : 3	1 : 2 : 12
1 : 6.5	1 : 2 : 4.5	1 : 2 : 18

Table 3. Theoretical densities for concrete batch formulas.[1]

Concrete Batch Formula (cement:sand:UO_2 aggregate)	Theoretical Concrete Density (g/cm^3)
1:2:3.5	4.70
1:2:6	5.53
1:2:9	6.25
1:2:12	6.79
1:2:15	7.20
1:2:18	7.53
1:2:21	7.80
1:2:24	8.02

chemically bound in the cement. It is noteworthy that the atomic hydrogen density decreases by a factor of 2.4 when going from a 1:2:3.5 to a 1:2:24 concrete.

The shielding calculations show that increasing the level of urania aggregate from a 1:2:3.5 mixture to a 1:2:9 reduces the concrete wall thickness (at the 200 mrem/hr limit) from 14 to 10 in. Further additions of urania from 1:2:9 to 1:2:24 only reduced the wall thickness from 10 to 8.5 in. The 1:2:15 and 1:2:18 mixture wall thicknesses were approximately 9.0 in. and only differed by a few tenths of an inch.

It appears that a mixture balancing shielding, workability, and strength should be near the 1:2:14 to 1:2:18 ratios. These correspond to cement:total aggregate values of about 1:5.5 to 1:6.5, compared to the more easily workable (cement rich) value of 1:3.5 (using a water/cement ratio of 0.4).

The static strength (compressive or tensile) and impact resistance required for various applications of DUCRETE have not yet been established. If the measured values for the urania aggregate concrete are lower than that required, modifications to increase the strength and impact toughness can be employed. These modifications might include fiber additives, fly ash or fine silica additives, reducing porosity, finely grinding the cement.

3.0 EXPERIMENTAL PROGRAM

3.1 Aggregate - UO_2, U_3O_8, Gravel, and Iron-Enriched Basalt

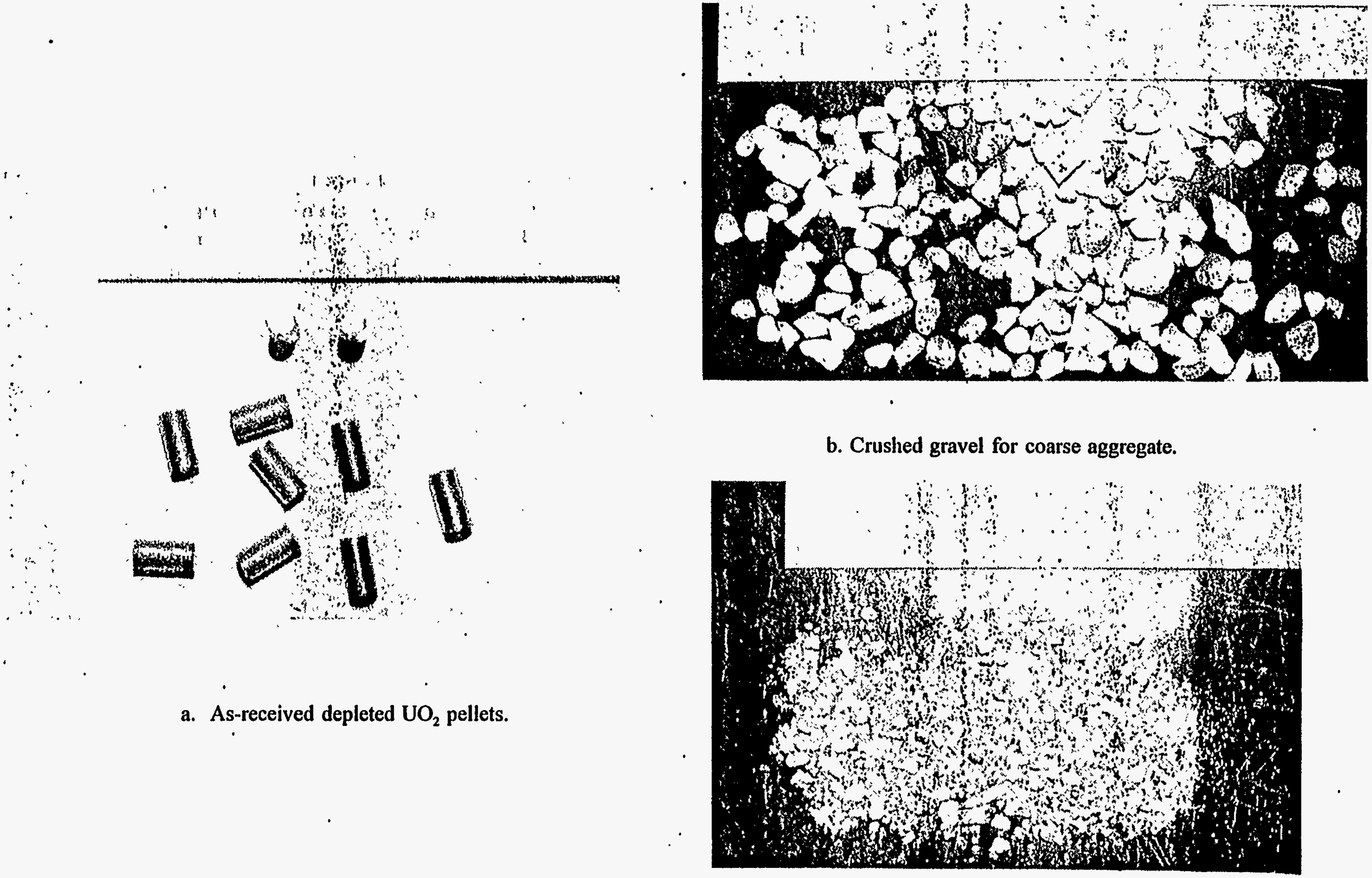
Depleted UO_2 pellets were received from Oak Ridge National Laboratory (ORNL) in stainless steel tubing. These pellets were sintered to be very dense with a hard, smooth surface and were 1/4 in. in diameter x 1/2 in. long. The pellets were removed from the tubing, cleaned, and directly used as aggregate. The pellets were not ground into smaller pieces because the larger, more regular pieces were predicted to enhance the workability. Figure 5a shows the UO_2 pellets.

It was decided to conduct control experiments with gravel (quartzite type) using equivalent cement:sand:gravel mixtures and the same water/cement ratio, cement:aggregate volumes, mixing techniques, etc. as used for the UO_2 aggregate concrete. Crushed gravel aggregate was obtained locally[b] and screened to a minus 3/8 in. to plus 4 mesh (0.110 in.) size fraction for use in the reference samples. This gravel was very irregular in shape with rough surfaces. Figure 5b shows the coarse (gravel) aggregate.

Depleted U_3O_8 was received as dense sintered plates (1/4 in. thick) from Argonne National Laboratory (West). Verbal information indicated that these plates were fabricated by Babcock & Wilcox Co. in Lynchburg, VA. The plates were fractured into irregular, block-like pieces and screened to a minus 1/4 in. to plus 4 mesh size fraction.

The iron-enriched basalt (IEB) was a synthetic mineral analyzed (in weight percent) as: 32.6 $Si0_2$, 5.20 Al_20_3, 16.4 FeO, 0.79 Fe_2O_3, 6.70 Ca0, 2.77 MgO, 2.86 N_2O, 1.46 K_2O, 21.4 $Ti0_2$, and 9.91 ZrO_2. This mineral was created by first arc melting all of the components except TiO_2 and ZrO_2.

b. The coarse aggregate (gravel) was analyzed using petrographic criteria as: Quartz Rock, 86.3 wt%; Granite/Granodiorite, 2.32 wt%; Obsidian, 4.85 wt%; Friable Sandstone, 3.86 wt%; Unknown non-silicate, 2.69 wt%. The "quartz rock" category included all non-friable particles containing more than 95 vol% quartz. The particles were very diverse in type of quartz and shape, which ranged from well-rounded through angular to platy. Quartz types included single quartz fragments of probable igneous origin, chalcedony, metasandstone in which the original sand particles were recognized, quartzite in which the original sand grains could not be distinguished, and others of unknown origin. The "Granite/Granodiorite" category was igneous rock containing quartz and feldspar with a few percent amphibole. The "Obsidian" category was made up of abraded, well-rounded particles of hard, black, vitreous material with conchoidal fracture (probably glass). The "Unknown" class was made up of material softer than stainless steel and nonreactive with hydrochloric acid (XRD indicated a minor dolomite phase).



a. As-received depleted UO_2 pellets.

b. Crushed gravel for coarse aggregate.

c. Fine aggregate (sieved sand).

Figure 5. Aggregate--depleted UO_2 pellets, crushed gravel, and sand.

After cooling, the Ti and Zr additions were blended in, followed by remelting in crucibles at 1450°C in a resistance furnace and then slow cooling to enhance formation of a crystalline zirconolite ($CaZrTi_2O_7$) phase. The material was then crushed and screened to a minus 1/4 in. to plus 4 mesh size fraction.

3.2 Sand

Surface dry, clean sand of local origin was used. The sand was sieved to a size fraction of minus 7 (0.110 in.) to plus 50 (0.0117 in.) mesh. Figure 5c shows the fine aggregate (sand). For U_3O_8 sand, the small fractions (minus 7 to plus 50 mesh) left over from the grinding of dense plates were used.

3.3 Mixing the Concrete

Ordinary Type I portland cement[b] was used. The batches were mixed using a planetary shear-type mixer (Hobart Model 330). The batches were mixed for approximately 2 to 5 min. Some minor fracturing of the aggregate occurred during this process. Eight batches were mixed according to weight fractions shown in Table 4.

The sand and cement were dry mixed together, followed by addition of either the gravel or UO_2 pellets. Once thoroughly mixed, the water was added, beginning at a water/cement weight ratio of 0.3 slowly increasing to slightly over 0.4 as dictated by workability. An organic surfactant/deflocculant[c]

Table 4. Batch formulas ratios (by weight).

cement:sand:gravel	cement:sand:UO_2 chunks
1 : 2 : 1.5	1 : 2 : 6
1 : 2 : 3	1 : 2 : 12
1 : 1.5 : 3.5	1 : 1.5 : 14
1 : 2 : 4.5	1 : 2 : 18

b. Ash Grove Cement West, Inc., Inkom, Idaho 83245. Complies to the following Standards: ASTM C 150-83a, AASHTO M85-79I, Federal Spec. SS-C-1960/3B. Chemical composition: SiO_2 21.79%, Al_2O_3 4.31%, Fe_2O_3 2.96%, CaO 63.30%, MgO 2.98%, SO_3 2.53 %, LOI 1.28 %, Insoluble residue 0.25%, Total alkalies (as Na_2O) 0.54 %.; C_3S 51.6%, C_2S 23.6%, C_3A 6.4%, C_4AF 9.0%.

c. PSI-400N, a water-reducing admixture manufactured by the Chemical Division of Gifford-Hill & Co, Inc., 300 East John W. Carpenter Freeway, Irving, Texas 75062. PSI-400N is formulated to comply with *Specifications of Admixtures*, ASTM Designation 494, Type A.

was admixed to the water to reduce the amount of water needed for good workability. No air entraining agents were added.

3.4 Cast the Concrete into Molds

The wet concrete was placed into thick-walled plastic molds. The workability was sufficient for the wet concrete to be hand placed (with some rodding) and vibrated into the mold without any large gaps. Specimens of the following types were fabricated:

(a) 2 in. diameter x 4 in. high for compression testing
(b) 2 in. diameter x 2 in. high for "Brazilian" diametral tensile testing.

Due to the limited amount of sintered UO_2 pellets available, only two samples of each type were cast for a given concrete composition.

3.5 The Concrete Was Cured

The samples were cured according to ASTM Standard C 192, *Method of Making and Curing Concrete Test Specimens in the Laboratory*, i.e., held at room temperature in water for the desired time (7, 28, or 90 days). This process is shown in Figure 6.

3.6 Sulfur End Caps

Sulfur end caps were cast onto the 2 in. diameter x 4 in. high compression specimens before testing to provide flat, parallel ends for testing (30 samples). This was done according to ASTM Standard C 192, *Standard Method of Making and Curing Concrete Test Specimens in the Laboratory*, and C 617, *Practice for Capping Cylindrical Concrete Specimens*.

3.7 Strength Tests

The concrete samples were broken using an Instron test machine. The 2 in. diameter x 4 in. high specimens were tested in compression according to ASTM C 39-72, *Compressive Strength of*

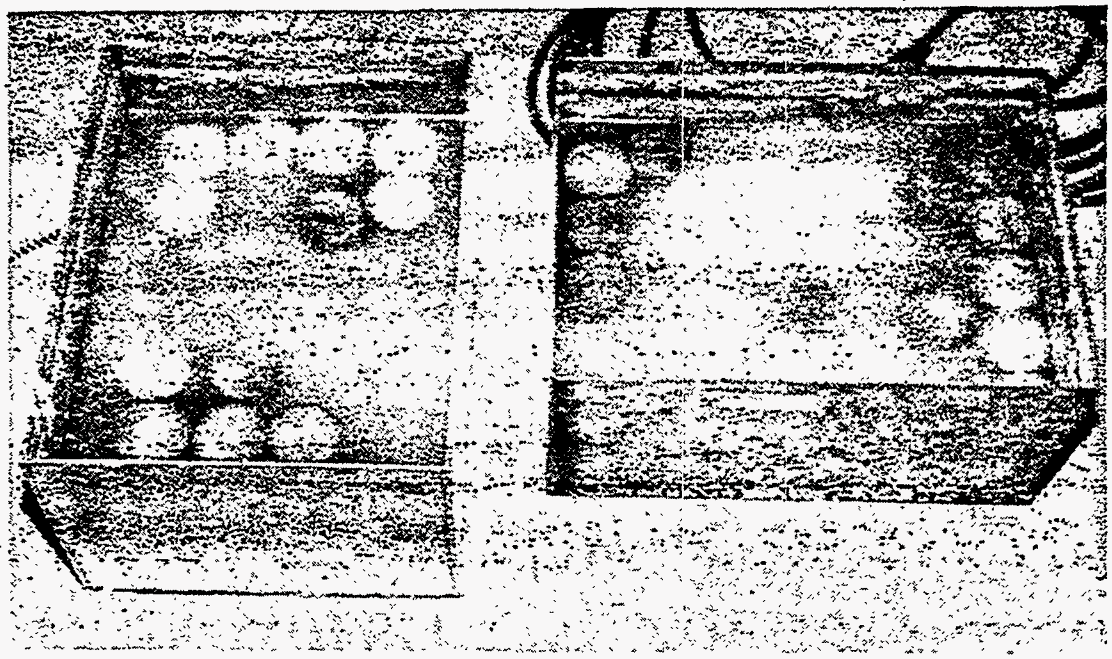


Figure 6. Concrete test specimens in curing tank.

Cylindrical Concrete Specimens, which specifies a spherical bearing block to minimize shear stresses at the end caps. The compression testing is shown in Figure 7.

The 2 in. diameter x 2 in. high specimens were tested using the Brazilian test. For this test, the disks are placed on edge and loaded in compression and the failure load, P, noted. The splitting tensile strength S_T is given by

$$S_T = \frac{2P}{\pi t d}$$

where

t = thickness of the disk
d = disk diameter.

The diametral Brazilian tension test is shown in Figure 8.

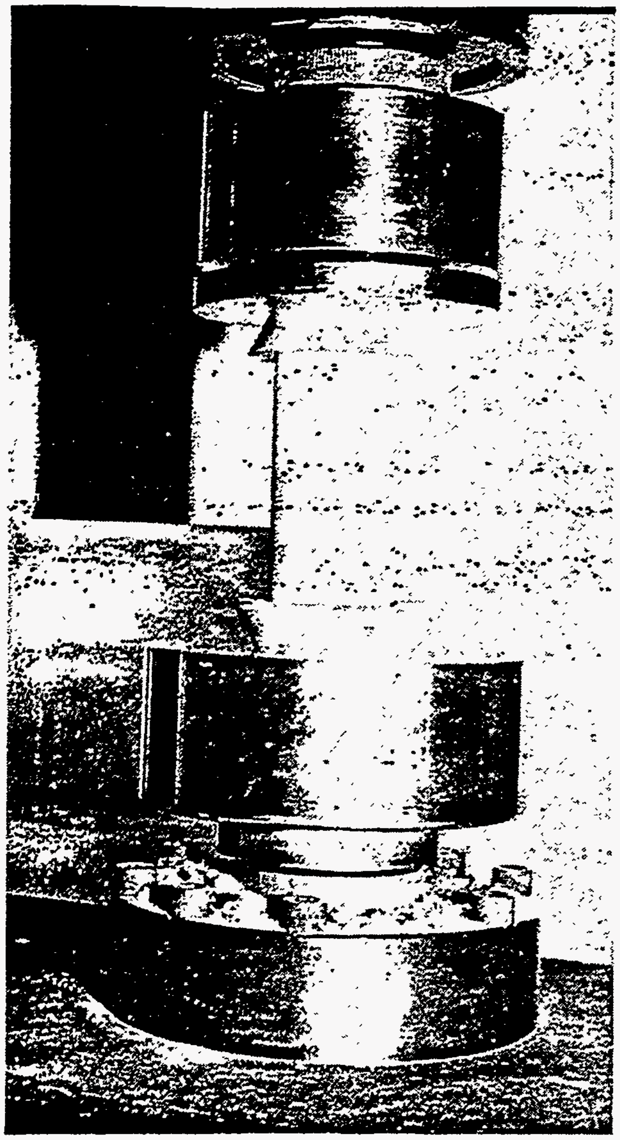


Figure 7. Compression testing of concrete specimens (note sulfur end caps).

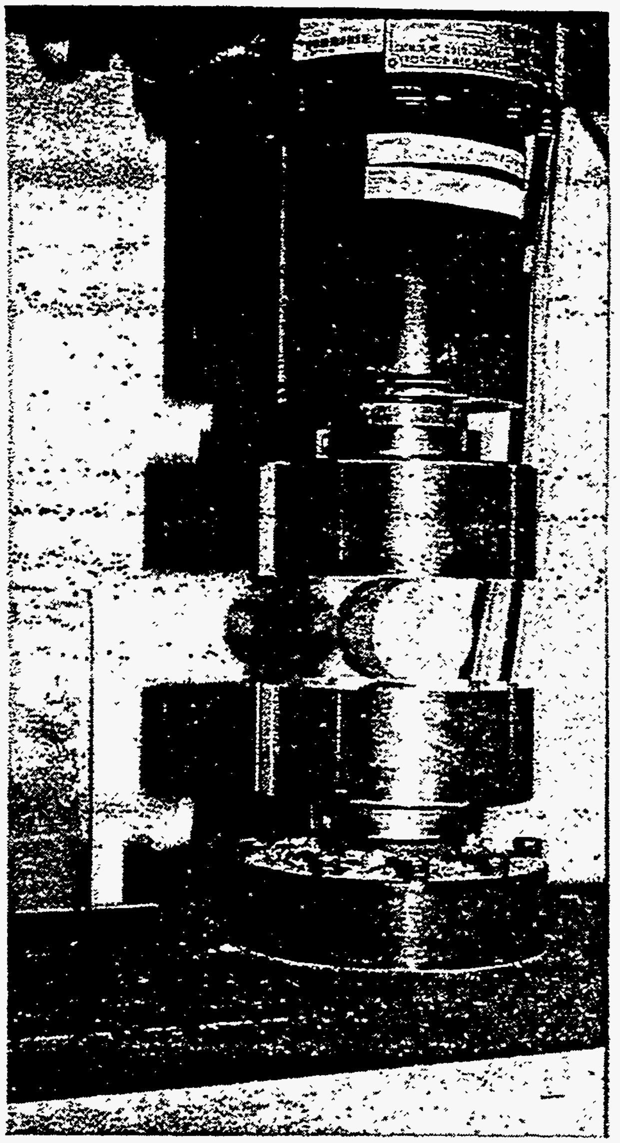


Figure 8. Tensile testing of concrete specimens using diametral "Brazilian" disk test.

3.8 High-Temperature Exposure Test

All of the samples were cured for 7 days at room temperature prior to the high-temperature exposure. The concrete samples were placed in a rack in an environmental chamber. A flowing atmosphere of air, humidified by bubbling through room temperature water, was provided. Since the chamber was not completely sealed, the pressure was not allowed to exceed one atmosphere and, therefore, at temperatures over approximately 100°C the exposure was to unsaturated steam (pressures did not follow the steam tables).

3.9 Characterization

Macro photos of the as-fabricated and broken samples were taken, and some test samples were cut and polished for optical micrography.

4.0 EXPERIMENTAL RESULTS

The as-cast reference gravel samples for mixtures 1:2:1.5, 1:2:3, 1:1.5:3.5, 1:2:4.5 are shown in Figures 9a through d, respectively. The UO_2 aggregate samples for the corresponding mixtures of 1:2:6, 1:2:12, 1:1.5:14, and 1:2:18 are shown in Figures 10a through d, respectively.

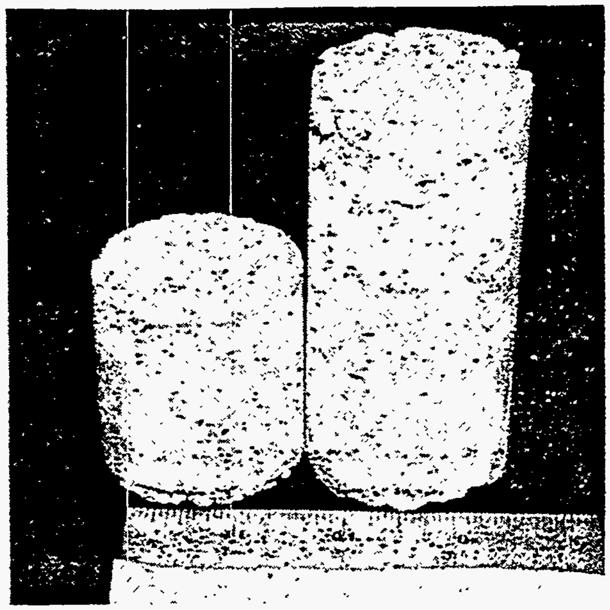
The 1:2:1.5 and 1:2:3 gravel samples had good workability and cast easily (although there was very little slump). The 1:2:4.5 sample was very "dry" and, besides the vibration, had to be "rodded" into place. The resultant sample had a rough surface appearance with a significant amount of gaps. The 1:1.5:3.5 samples were much easier to cast than the 1:2:4.5 sample and had less surface roughness.

The UO_2 aggregate concretes were more workable than the corresponding gravel concretes. This is illustrated by less roughness on the walls of the as-cast specimens. We were concerned that at the high UO_2 loadings the heavy aggregate would segregate to the bottom of the sample; this did not occur. In the 1:2:18 UO_2 sample there was such a high volume fraction (approx. 70%) of aggregate that it was locked in place and the cement/sand/water fraction tended to settle to the bottom. This was different than the 1:2:4.5 gravel samples where there was little tendency for any segregation of components.

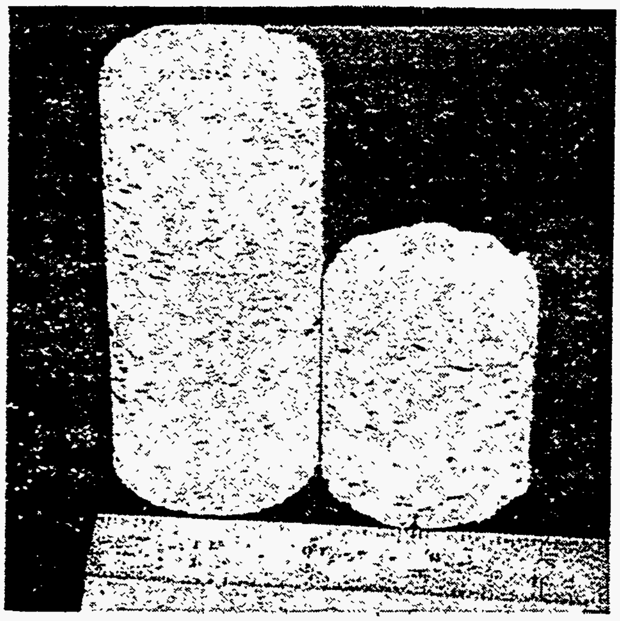
Figure 11 shows typical compression and tensile failure crack patterns for 1:2:6 UO_2 samples; Figure 12 is a closer view of the fracture surfaces from the Brazilian tensile test for a 1:2:6 UO_2 sample. Figure 13a illustrates the fracture patterns for 1:2:1.5 gravel aggregate concrete tested in compression and tension; Figure 13b is a closer view of failed gravel-rich (1:2:4.5) specimens. Tables 5 and 6 show the measured density and strength results.

Table 7 gives the test results from the elevated temperature exposure study. There was no visible damage to any of the concretes at temperatures between 90 and 150°C. When exposed at 250°C for 14 days, there was no visible damage to the reference concrete but the DUCRETE made with U_3O_8 aggregate cracked as shown in Figures 14a and b (closeup). The damage at 250°C for 14 days to the UO_2 DUCRETE is shown in Figure 15 - the DUCRETE crumbled to the bottom of the chamber. The UO_2 pellets were integral and solid, but the surface changed from brown to dusty black.

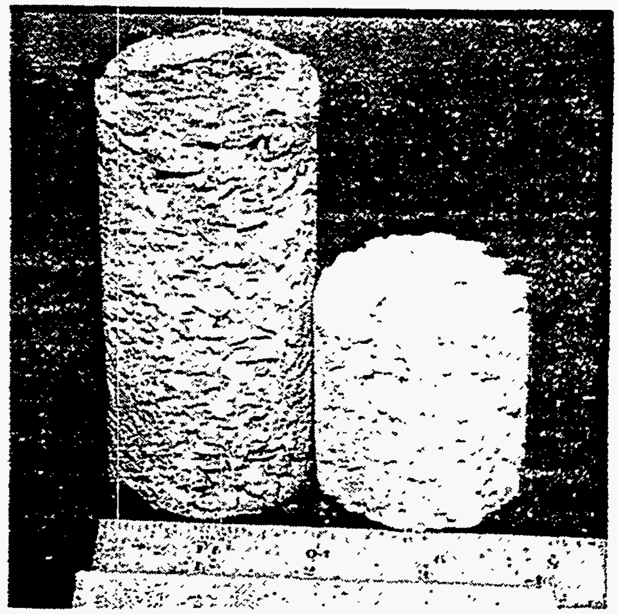
a. 1:2:1.5



b. 1:2:3

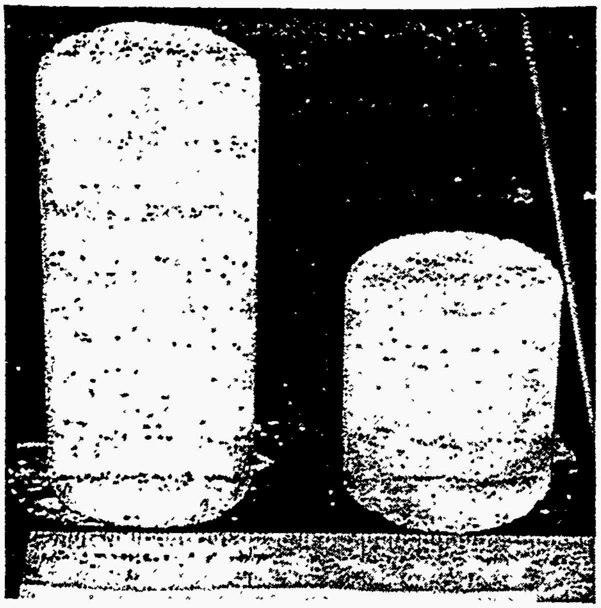


c. 1:1.5:3.5

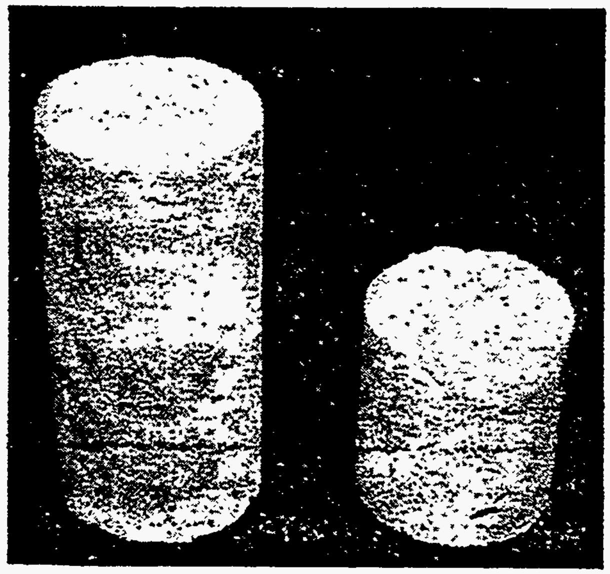


d. 1:2:4.5

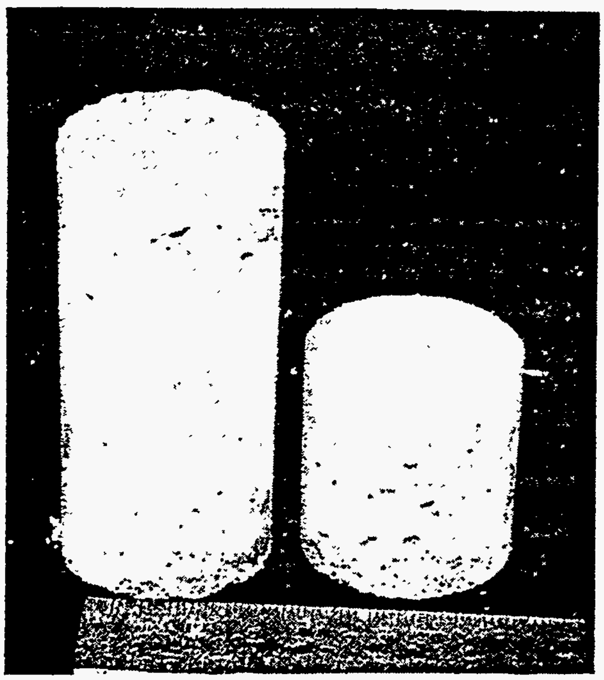
Figure 9. As-cast reference gravel aggregate concrete--mixtures 1:2:1.5, 1:2:3, 1:1.5:3.5, and 1:2:4.5.



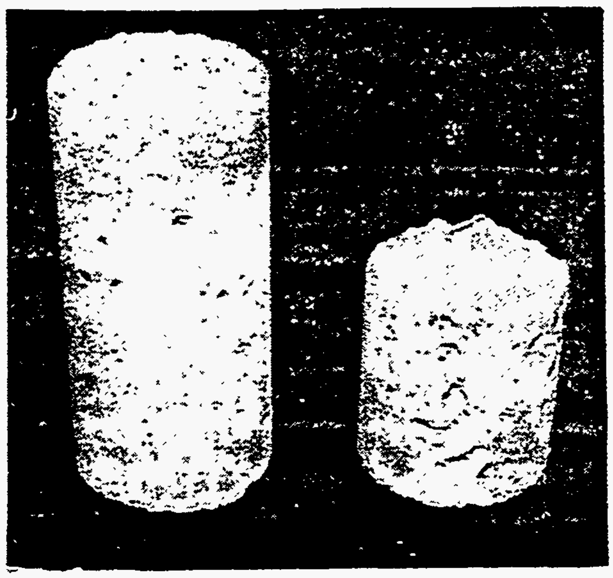
a. 1:2:6



b. 1:2:12



c. 1:1.5:14

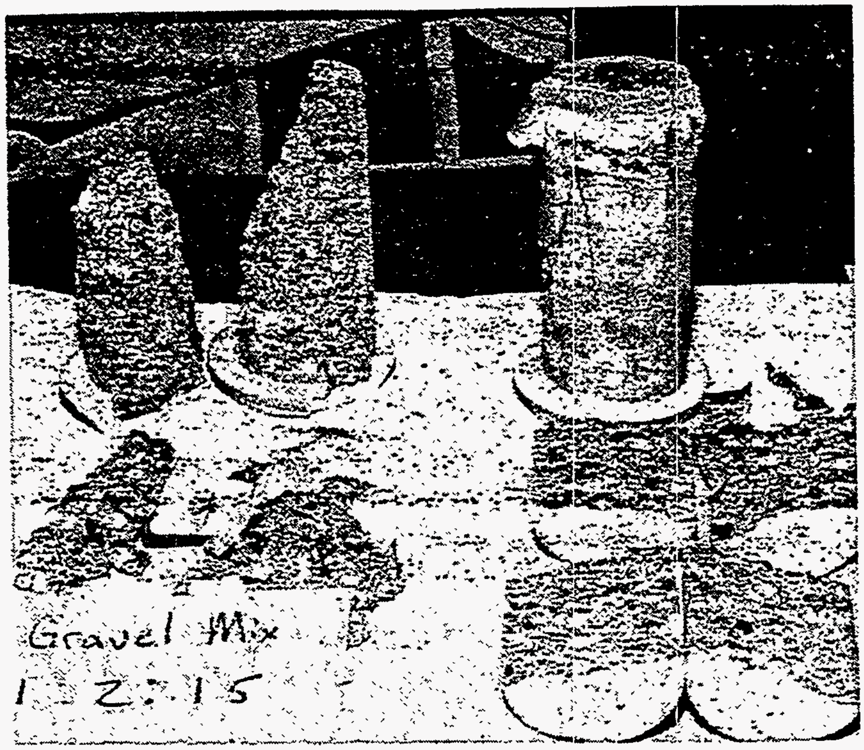


d. 1:2:18

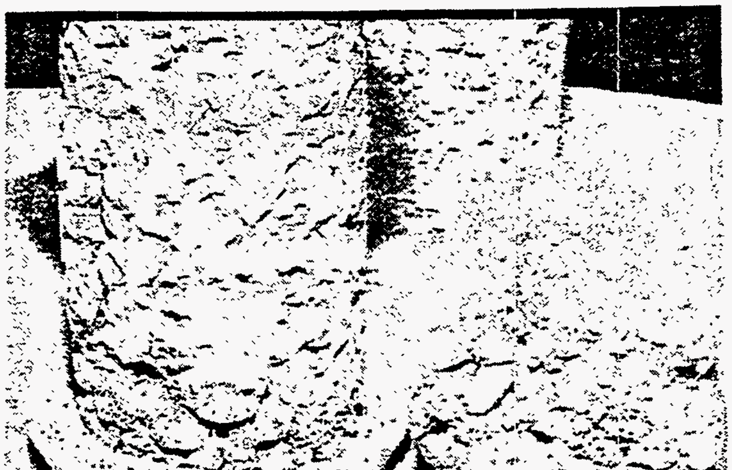
Figure 10. As-cast DUCRETE UO_2 aggregate concrete--mixtures 1:2:6, 1:2:12, 1:1.5:14, and 1:2:18.

Figure 11. Failed 1:2:6 UO_2 concrete (two compression, one tensile specimen).

Figure 12. Closeup view of tensile fracture surfaces of 1:2:6 UO_2 tensile specimen.



a. 1:2:1.5 gravel aggregate concrete (two compression, two tensile specimens)



b. Closeup view of failed 1:2:4.5 gravel aggregate concrete (note surface roughness)

Figure 13. Failed gravel aggregate concrete.

Table 5. UO_2 DUCRETE and reference concrete properties.

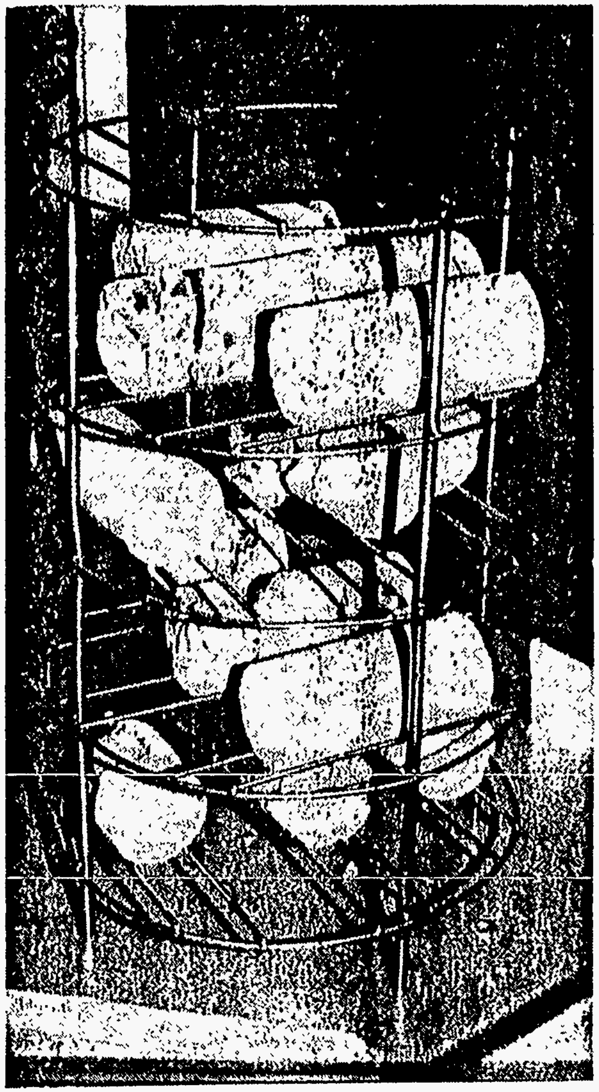
Mass Ratio of Mixture	W/C ratio	PSI-400N (oz/100 lbs of cement)	Density (g/cm^3)	Compressive Strength (psi)	Brazilian Test Tensile Strength (psi)
After 7 days of curing					
1:2:1.5	0.428	0.0323	2.28	6,671	647.2
1:2:6 (UO_2)	0.400	0.2974	4.60	4,304	541.6
1:2:3	0.447	0.0405	2.29	6,263	596.2
1:2:12 (UO_2)	0.495	2.949	5.89	4,781	526.0
1:1.5:3.5	0.400	2.948	2.21	4,562	449.3
1:1.5:14.2 (UO_2)	0.450	2.947	6.27	4,228	359.3
1:1.5:10.0 (U_3O_8)	0.500	2.994	4.44	3,594	328.0
1:2:4.5	0.459	0.0490	2.11	3,746	438.0
1:2:18 (UO_2)	0.450	0.4498	6.44	3,097	435.1
After 28 days of curing					
1:2:1.5	0.428	0.0323	2.28	6,188	690.0
1:2:6 (UO_2)	0.400	0.2974	4.60	4,096	573.5
1:2:3	0.447	0.0405	2.29	5,112	659.0
1:2:12 (UO_2)	0.495	2.949	5.89	5,397	426.5
1:1.5:3.5	0.400	2.948	2.21	5,446	656.5
1:1.5:14.2 (UO_2)	0.450	2.947	6.27	3,565	473.0
1:2:4.5	0.459	0.0490	2.11	4,125	387.0
1:2:18 (UO_2)	0.450	0.4498	6.44	3,307	425.0
After 90 days of curing					
1:2:1.5	0.428	0.0323	2.28	4,664	762.0
1:2:6 (UO_2)	0.400	0.2974	4.60	5,223	621.5
1:2:3	0.447	0.0405	2.29	5,668	548.0
1:2:12 (UO_2)	0.495	2.949	5.89	5,765	467.0
1:1.5:3.5	0.400	2.948	2.21	5,756	549.5
1:1.5:14.2 (UO_2)	0.450	2.947	6.27	4,611	431.5
1:2:4.5	0.459	0.0490	2.11	4,213	432.5
1:2:18 (UO_2)	0.450	0.4498	6.44	4,379	392.0

Table 6. Iron-enriched basalt aggregate concrete properties compared to reference concrete.

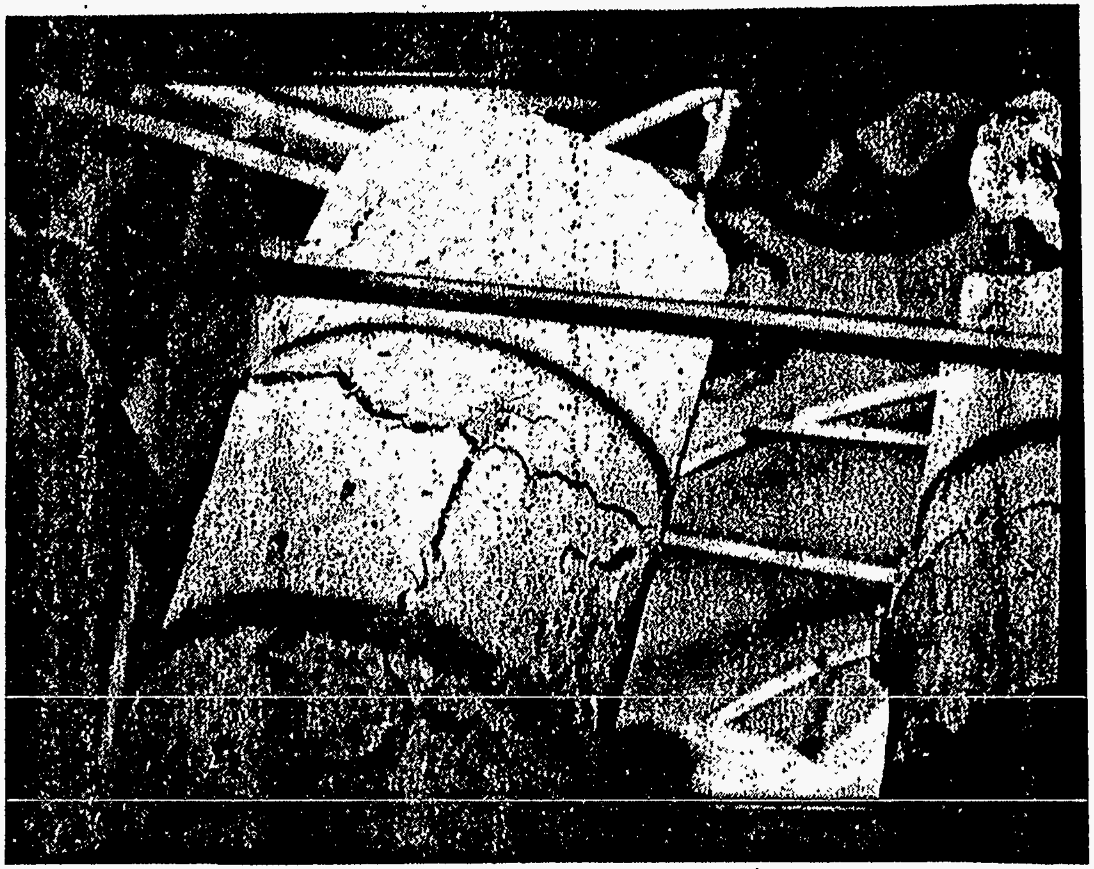
Mass Ratio of Mixture	W/C ratio	PSI-400N (oz/100 lbs of Cement)	Density (g/cm^3)	Compressive Strength (psi)	Brazilian Test Tensile Strength (psi)
			After 7 days of curing		
1:2:1.5	0.428	0.0323	2.28	6,671	647.2
1:2:1.7 (IEB)	0.401	0.2958		3,784	360.0
1:2:3	0.447	0.0405	2.29	6,263	596.2
1:2:3.4 (IEB)	0.405	2.930		4,002	459.0
1:1.5:3.5	0.400	2.948	2.21	4,562	449.3
1:1.5:4.0 (IEB)	0.498	2.948		3,234	425.5
1:2:4.5	0.459	0.0490	2.11	3,746	438.0
1:2:5.1 (IEB)	0.499	2.931		3,072	401.5
			After 28 days of curing		
1:2:1.5	0.428	0.0323	2.28	6,188	690.0
1:2:1.7 (IEB)	0.401	0.2958		5,765	621.0
1:2:3	0.447	0.0405	2.29	5,112	659.0
1:2:3.4 (IEB)	0.405	2.930		4,251	669.0
1:1.5:3.5	0.400	2.948	2.21	5,446	656.5
1:1.5:4.0 (IEB)	0.498	2.948		4,074	543.5
1:2:4.5	0.459	0.0490	2.11	4,125	387.0
1:2:5.1 (IEB)	0.499	2.931		3,530	480.5

Table 7. Concrete properties - oxidation study.

Aggregate Type	Mass Ratio of Mixture	W/C ratio	PSI-400N (oz/100 lbs of cement)	Density (g/cm^3)	Compressive Strength (psi)/Standard Deviation (psi)	Brazilian Test Tensile Strength (psi)/ Standard Deviation (psi)
			7 day, Room Temperature			
Gravel	1:1.5:3.5	0.400	2.948	2.21	4,562 / 43	449.3 / 41
UO_2	1:1.5:14.2	0.450	2.947	6.27	4,228 / 424	359.3 / 126
			14 day, 90°C			
Gravel	1:1.5:3.5	0.401	2.993		4,458 / 1685	
UO_2	1:1.5:14.2	0.450	2.947		4,649 / 765	650.5 / 15
			28 day, 90°C			
Gravel	1:1.5:3.5	0.401	2.993		5,037 / 628	
UO_2	1:1.5:14.2	0.450	2.947		4,246 / 2058	604.5 / 88
			14 day, 125°C			
Gravel	1:1.5:3.5	0.401	2.993		5,169 / 8	
UO_2	1:1.5:14.2	0.450	2.947		4,947 / 600	557.5 / 29
			28 day, 125°C			
Gravel	1:1.5:3.5	0.401	2.993		3,937 / 647	
UO_2	1:1.5:14.2	0.405	2.947		3,035 / 684	556.0 / 50
			14 day, 150°C			
Gravel	1:1.5:3.5	0.401	2.993		5,217 / 349	
UO_2	1:1.5:14.2	0.405	2.947		3,479 / 737	658.5 / 16
			28 day, 150°C			
Gravel	1:1.5:3.5	0.401	2.993		5,435 / 177	
UO_2	1:1.5:14.2	0.405	2.947		3,785 / 1351	639.0 / 5
			14 day, 250°C			
Gravel	1:1.5:3.5	0.401	2.993		3,271 / 554	
UO_2	1:1.5:14.2	0.405	2.947	NA	Disintegrated	
U_3O_8	1:1.5:10	0.500	2.984	NA	Deep Cracks	



a. DUCRETE and reference concrete. Note the DUCRETE is cracked while the reference concrete is intact.



b. Close-up of DUCRETE. Surface cracks appear to originate from pieces of U_3O_8 aggregate.

Figure 14. DUCRETE made with U_3O_8 aggregate and reference concrete after exposure to 250°C for 14 days.

Figure 15. DUCRETE made with UO_2 aggregate after exposure to 250°C for 14 days. The DUCRETE completely disintegrated although the UO_2 pellets are intact. The pellets had a dusty appearance.

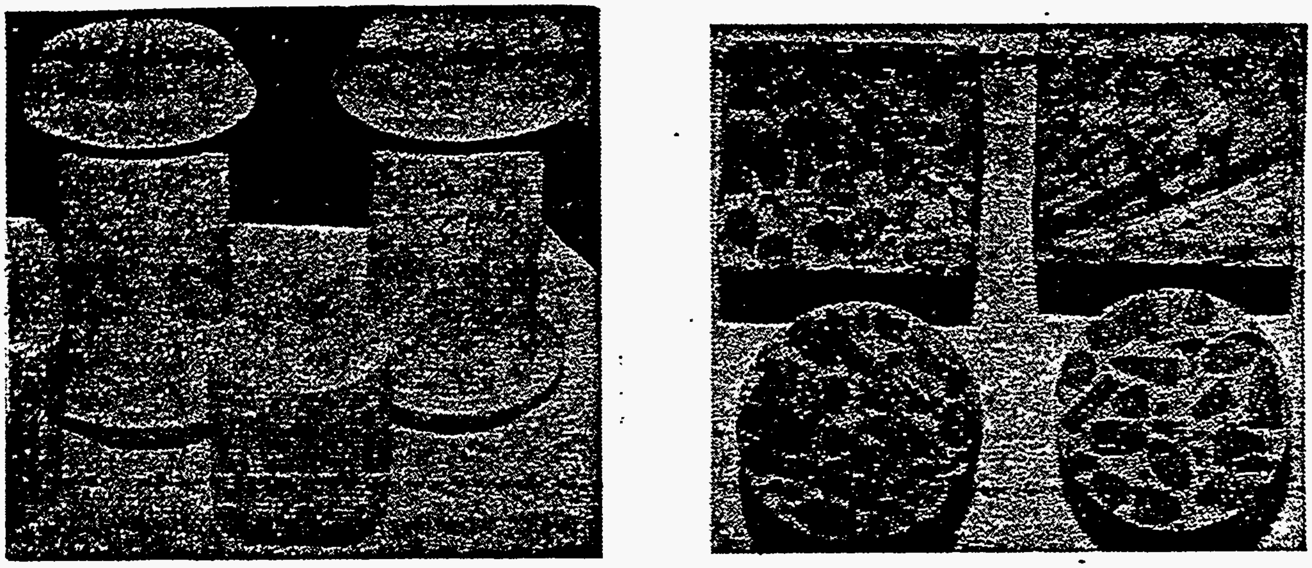
5.0 DISCUSSION OF RESULTS

As expected, the density of DUCRETE was much higher than that of ordinary concrete. Using a high loading of UO_2 aggregate (1:2:18), the density was 6.44 g/cm^3, compared to 2.11 g/cm^3 for the equivalent gravel aggregate concrete. The measured density values of the gravel concrete specimens were in the range predicted.. The densities of the UO_2 aggregate concrete specimens were slightly lower than the theoretical value used in the shielding calculations. This probably is due to the assumptions made during the theoretical calculation and some porosity evident in the concrete.

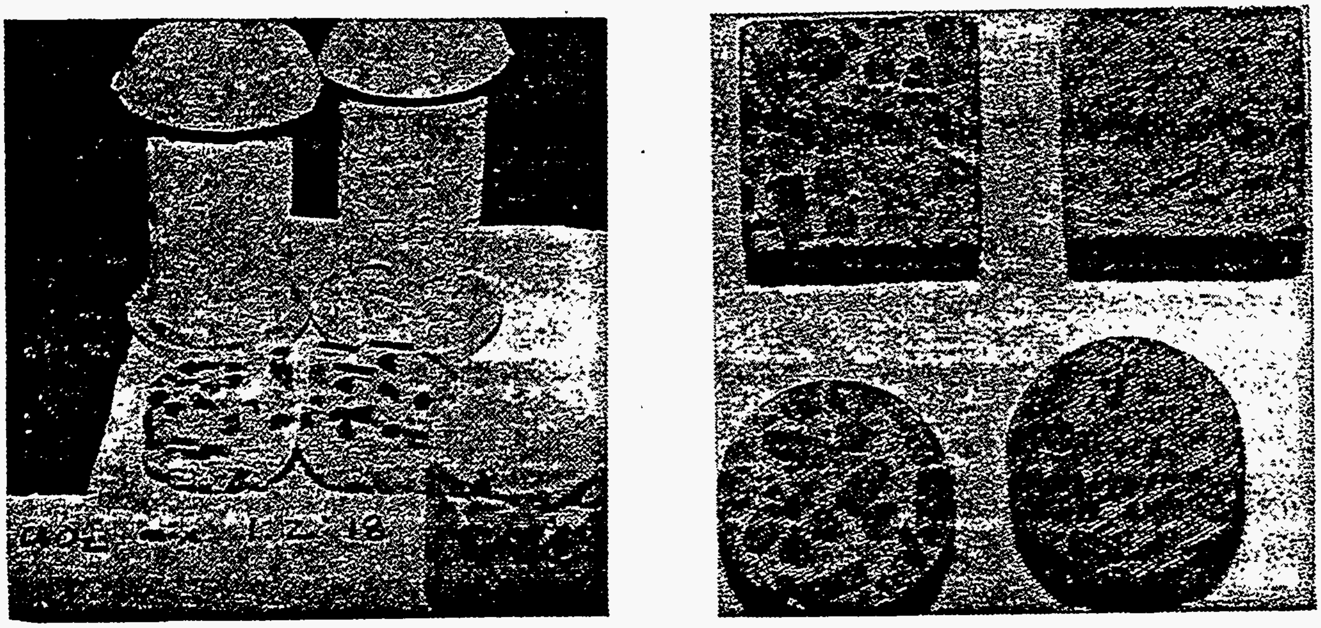
The mixing and casting results suggest that the regular shape and smooth, rounded surface of the UO_2 aggregate samples aid in the workability when compared to samples that used the slightly smaller but very irregularly-shaped gravel aggregate. The IEB aggregate batches were also very difficult to mix (attributed to the irregular, flat-shaped aggregate flakes).

The higher gravel and UO_2 aggregate loadings (1:2:4.5 and 1:2:18) were very difficult to mix by hand in trial batches, but were successfully mixed using the high-shear planetary mixer. Problems in getting a homogeneous mix with these high loadings would be predicted using an ordinary rotary drum cement mixer. In addition, cement/sand/water segregation was observed for the 1:2:18 mixture. The 1:1.5:3.5 and 1:1.5:14 UO_2 mixtures showed better mixing and casting characteristics. This is evidenced by the smoother external surfaces of the castings as shown in Figures 16 and 17. Also note the lack of large porosity in the interior of both the 1:1.5:14 and 1:2:18 mixtures, even though the 1:2:18 sample has a very rough exterior.

The strength values were averaged over only two specimens (due to shortage of UO_2 aggregate) and thus should only be taken as a rough indicator of strength trends; a study with more data points would be preferred. All of the 7-day cured mixtures, including the DUCRETE, showed compression strengths that were about the same as those of ordinary construction grade concretes (3,000 to 6,000 psi). The strengths consistently decreased with increasing aggregate content. The UO_2-containing mixtures consistently showed slightly lower strengths than the equivalent gravel samples. The difference was smaller at high aggregate loadings; this is probably related to the smooth, regular shape of the UO_2 aggregate. The IEB aggregate concrete also showed reduced compressive and tensile strengths compared to the gravel-aggregate concrete. The IEB aggregate consisted of flat, irregular flakes of material.



1:1.5:14



1:2:18

Figure 16. Comparison of DUCRETE made with 1:1.5:14 and 1:2:18 mixtures of cement:sand:UO_2 aggregate. Note the rough exterior of the 1:2:18 mixture, although the sawed cross sections appear to have a minimal amount of large porosity.

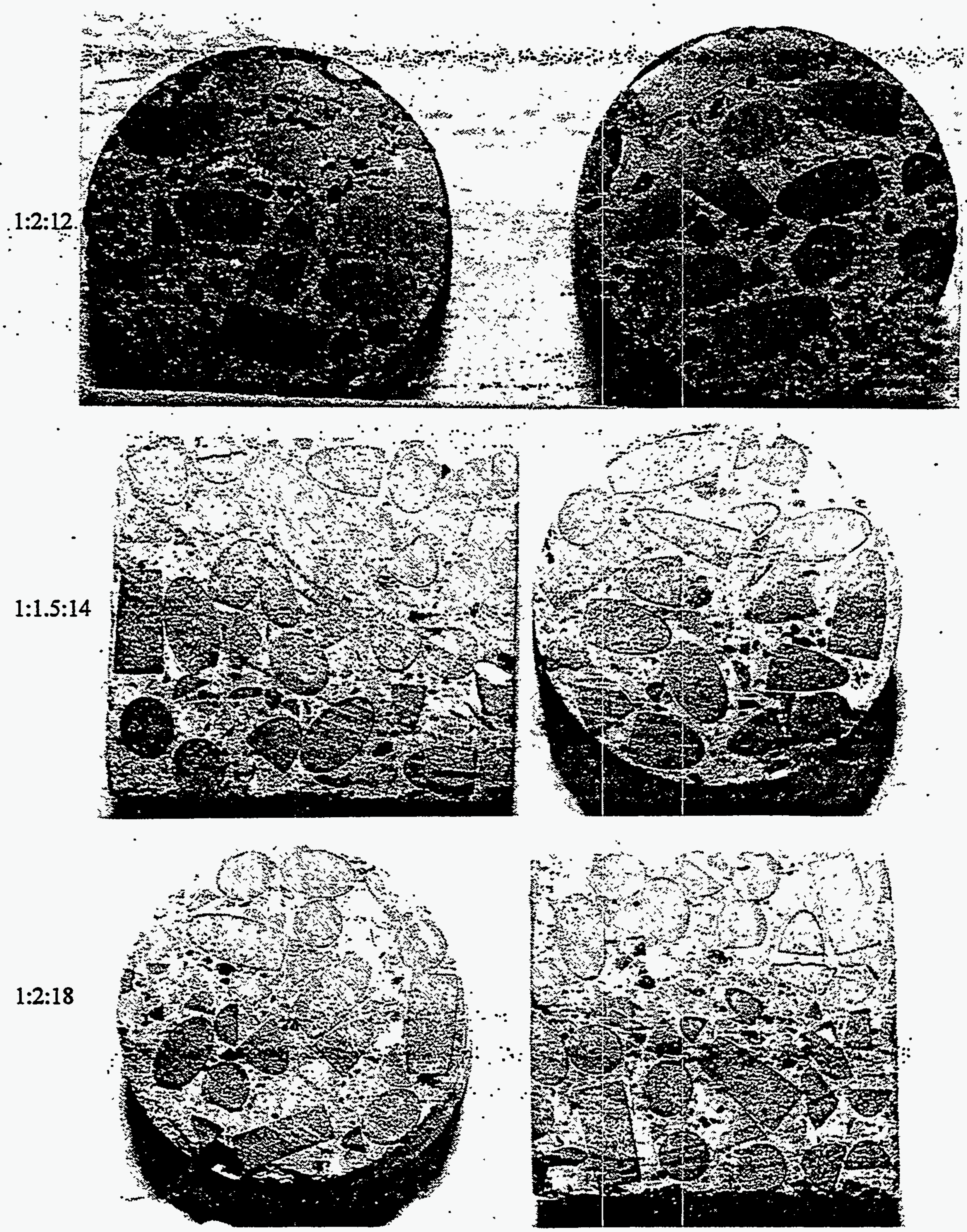


Figure 17. Sawed cross sections of DUCRETE made with increasing weight/volume fractions of UO_2 aggregate.

Close examination of the tensile fracture surfaces showed less interlocking and bonding of the sand/cement matrix to the UO_2 aggregate than to the gravel. As shown in Figure 18, when the long axis of the UO_2 pellet was perpendicular to the advancing crack, the UO_2 pellet would fracture; when the pellet was oblique or parallel to the crack, the fracture was along the interface. There was less of a tendency toward this type of cracking morphology with the gravel aggregate, where the fracture was smoother and a higher fraction of the gravel was fractured.

The tensile test values were approximately 10% of the compression values. The tensile strength of normal concrete is about 8% to 12% of the compressive strength and is often estimated as 5 to 7.5 times the square root of the compressive strength.[3]

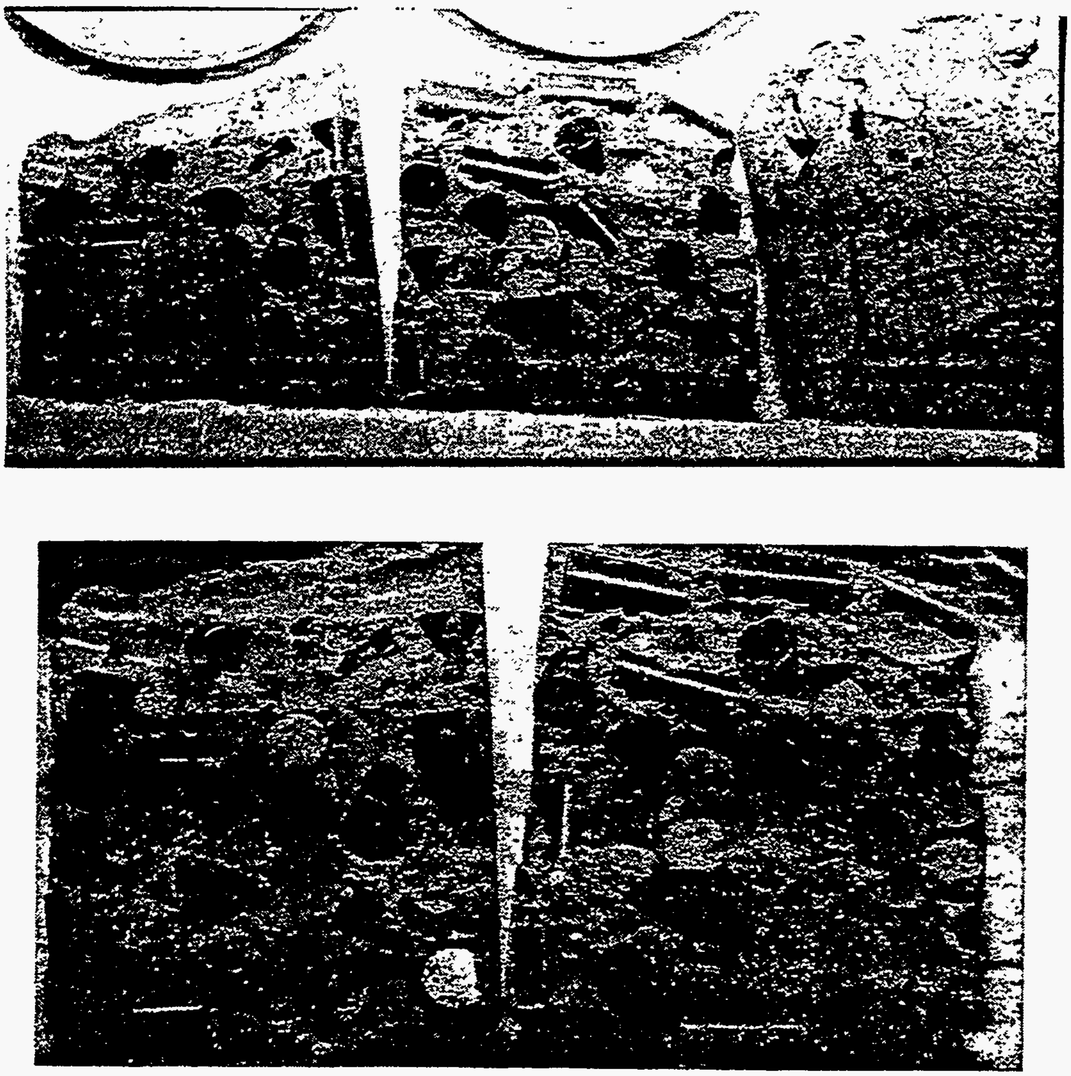


Figure 18. Fracture surfaces of DUCRETE made with UO_2 pellet aggregate (1:2:18 mixture).

The high-temperature exposure study was considered to be an "oxidation" study because of the easy access of air and water vapor to the aggregate through the open pores of the cement. There was water vapor available from water not reacted to form calcium silicate hydrate compounds and from water vapor in the atmosphere. The results of Table 7 should be interpreted very carefully. The tests were only expected to indicate general trends, since usually only two samples were broken per data point because there was not sufficient depleted uranium oxide aggregate to fabricate more samples. In addition to the small number of duplicate samples, ceramics are brittle materials and typically have a broad strength distribution curve due to a large variation in flaw sizes.[4] As a result, the standard deviation values for the tests are quite variable and sometimes very high.

Given a distribution of measurements that is approximately bell shaped, the interval of $\mu \pm \sigma$ contains about 68% of the measurements; 95% of the measurements are contained in $\mu \pm 2\sigma$. To increase our confidence that the mean value for a data point can be used to establish a trend, we should increase the number of samples measured. A minimum of 10 samples should be used to shrink envelope of the 95% confidence level.

Figure 19 shows the compressive strength data for the reference (gravel aggregate) concrete. The numbers by the data points are the number of days of exposure at the temperature shown on the ordinate. Error bars of $\pm 1\sigma$ are also indicated. The data points that do not appear to have error bars actually have standard deviations that are smaller than the size of the marker used for the data point. Other data points have very large standard deviations. However, a regression fit for the data indicates a general increase in the compression strength for temperatures up to 150°C and then a decrease in strength at 250°C. The 95% confidence envelope (curved lines) indicates that it is possible that the dependence could actually be flat (no change in mean strength up to 150°C) or very negative (if we had included the 250°C data point in the regression analysis).

Figure 20 is a plot of the compressive strength of concrete fabricated with depleted UO_2 pellets for aggregate. Standard deviations for some of these data are larger than for the reference concrete. The regression line indicates a slight decrease in strength from room temperature to 150°C. However, the 95% confidence level envelope shows the data could also support a flat dependence (no degradation of strength). The 250°C data were not used because the concrete crumbled. It was clear that a 250°C exposure for 14 days greatly harmed both the UO_2 and U_3O_8 aggregate concrete. The effect was greater for the UO_2 than for the U_3O_8. (Maximum long-term exposure temperatures for the concrete in spent nuclear fuel storage containers are expected to be 50 to 150°C.[5,6,7])

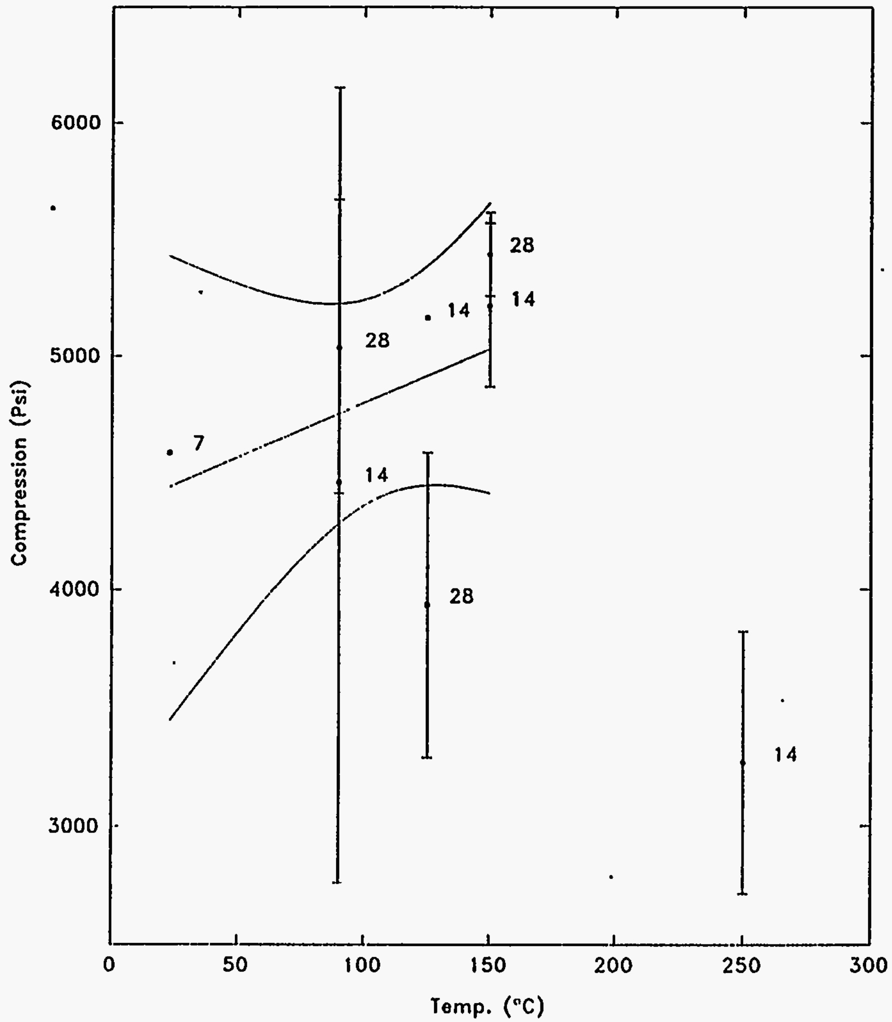


Figure 19. Compression strength test results for reference concrete exposed to various temperatures.

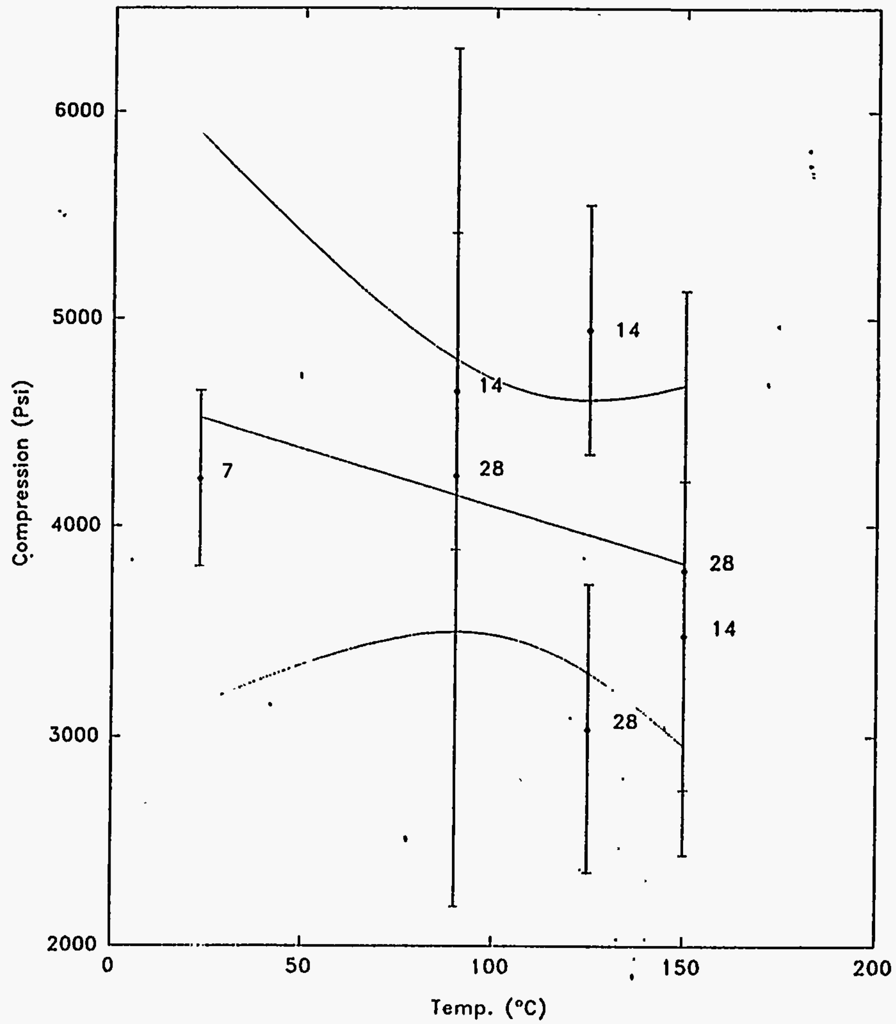


Figure 20. Compression strength data for DUCRETE (UO_2 aggregate) exposed to various temperatures. Data were not taken at 250°C because the samples had crumbled.

The numbers 7, 14, and 28 refer to days of exposure. Error bars of one standard deviation are shown (small errors are contained within the data point symbol). The two curved lines are the 95% confidence limits.

Figure 21 plots tensile (Brazilian method) strengths for UO_2 aggregate concrete. The standard deviations are quite small and the regression analysis definitely shows an increase in strength for temperatures up to 150°C. This can be attributed to an increase in creating hydrated bonds (accelerated curing) in the calcium silicate phases of the portland cement. It is possible that the tensile data are primarily a measure of the strength of the cement phase (cement plus sand), while the compression data are more of a reflection of the bond between the cement phase and the large aggregate.

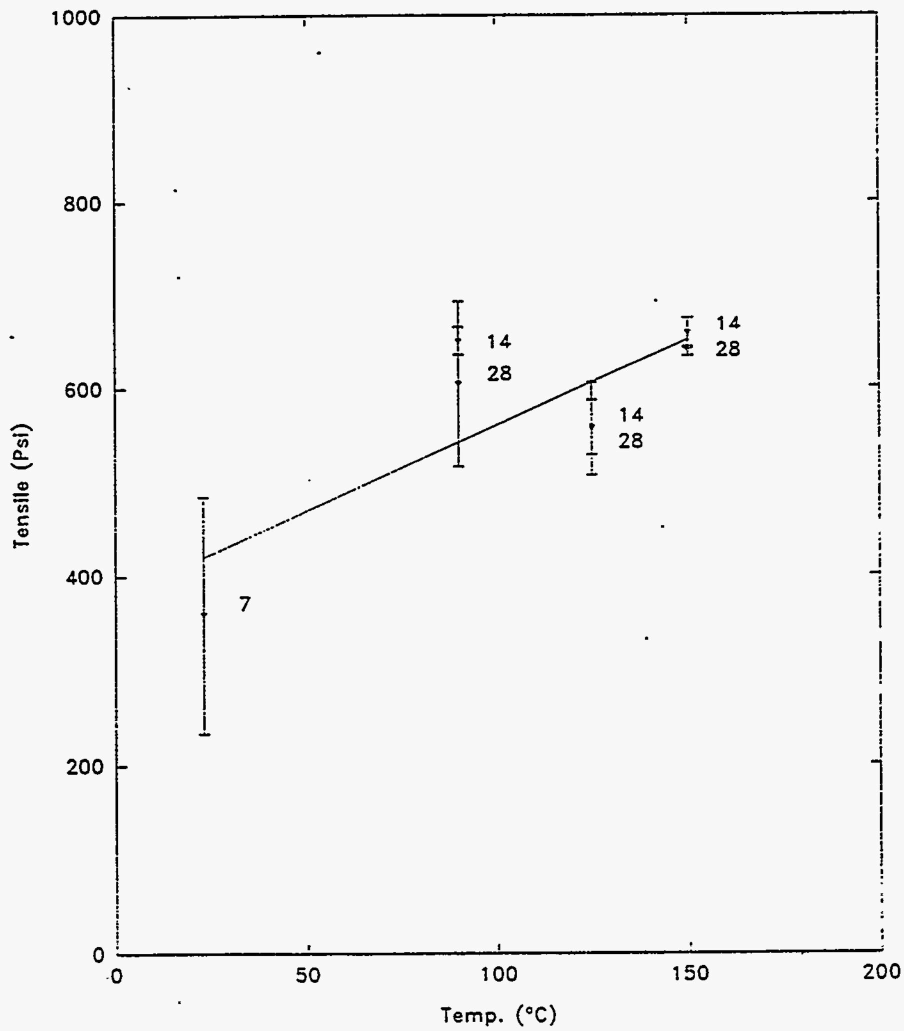


Figure 21. Tensile (Brazilian) strength data for DUCRETE (UO_2 aggregate) exposed to various temperatures.

6.0 CONCLUSIONS

The strength values for DUCRETE are in the range of typical construction grade concretes for an equivalent curing time (7 days). DUCRETE exhibits slightly lower (20.6% average) compression strength values than the equivalent gravel-aggregate concrete.

From a mixing and casting perspective, 1:1.5:14 is the highest UO_2 loading recommended for casting large structures. This mixture only showed a 7.3% reduction in compressive strength compared to the reference gravel-aggregate concrete.

Visual examinations found no deleterious interactions between the UO_2 pellet aggregate and the cement/sand/water matrix when cured for 7 days at room temperature. More samples (at least 10 per data point) need to be tested to narrow the standard deviations to better statistically determine if the mean compressive strengths are degrading at elevated temperatures. Analysis of data taken thus far, using two samples per data point, shows the possibility of a slight degradation in compressive strength for temperatures between 90°C and 150°C for times up to 28 days. The mean tensile strengths are increased by exposure to temperatures up to 150°C.

Reference concrete fabricated with gravel aggregate showed about a 1,300 psi decrease in mean compressive strength with exposure to temperatures of 250°C; equivalent samples fabricated using depleted uranium oxide aggregate either cracked or completed disintegrated when exposed to 250°C. This temperature is 100°C higher than the maximum temperature expected for the anticipated applications of DUCRETE for spent nuclear fuel storage or shipping.

7.0 REFERENCES

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6. *BR-100 Shipping Cask Preliminary Design Report*, 51-1177082-03, Babcock & Wilcox Fuel Co., Page II-3-11.

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